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The Mechanism of Decomposition of Azo Compounds. I. 1,1'-Azocyanocyclohexane and N-(1-Cyanocyclohexyl)-pentamethyleneketenimine

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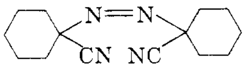
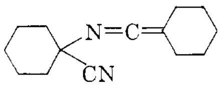
The rates of formation of N-(1-cyanocyclohexyl)-pentamethyleneketenimine (RR') from 1,1'-azocyanocyclohexane (RN_2R) have been followed at 80 and 100° with and without the presence of radical scavengers. The initial rate of formation of RR' is significantly decreased in the presence of scavengers. This provides evidence for the coexistence of two paths for the formation of RR'. We believe that one is by primary recombination of pairs of cyanocyclohexyl radicals (R·) in the solvent cage and that the other is by coupling of radicals which have been separated from their original partners by diffusion. The ketenimine has been isolated in pure form, and its rates of decomposition under various conditions have been found to follow first-order kinetics. The rate of decomposition of RR' is significantly accelerated in the presence of scavengers. This is consistent with a radical mechanism; the "free" R· which are scavenged are thereby prevented from coupling to regenerate RR'. The rates of decomposition of RN_2R at 80 and 100°, the efficiencies of radical production from both RN_2R and RR', and the rates of cumene oxidation initiated by RN_2R and RR' have also been studied. These data make possible a complete analysis of the distribution of radicals formed in the decomposition of RN_2R.

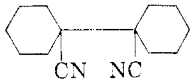
In this and the following paper,[1] studies of the thermal decomposition of two azonitriles and the related ketenimines will be presented. Kinetic equations developed in this paper will be used again in the second paper, and the latter will contain a general discussion of the status of the theory of cage effects as applied to these systems. This paper concerns the decomposition of 1,1'-azocyanocyclohexane (RN_2R, I) and N-(1-cyanocyclohexyl)-pentamethyleneketenimine (RR', II). In some respects the system is more attractive for study than α,α'-azoisobutyronitrile (ABN). This is partly due to the fact that some of the key relationships are easier to measure because of differences in relative reactivities and partly due to the fact that II is a stable, crystalline compound at room temperature.



I (RN_2R)



II (RR')



III (RR)

The rates of decomposition of RN_2R in xylene[2] and toluene[3] have previously been measured, and the stable product III was isolated in nearly quantitative yield. Considerable amounts of RR' are formed from RN_2R during the early stages of the decomposition. The technique for isolation of RR' was similar to that developed for isolation of the ketenimine from ABN.[4] We were also aided by advice from Walling and Rivin who have also prepared and studied II at Columbia University.[5]

Results

Decomposition of RN_2R.—The first-order rate of decomposition of I in chlorobenzene at 80° has been measured in two ways: (1) by monitoring nitrogen evolution and (2) spectrophotometrically using the absorption of RN_2R at 3700 Å. Good, reproducible rate constants were obtained which agreed well with those calculated from the manometric runs. Only the spectrophotometric method was used at 100°. The results are summarized in Table I. It should be pointed out that careful exclusion of oxygen is necessary in order to obtain good results by the spectrophotometric method.

Formation of RR' from RN_2R.—The production of II from I was followed by measurement, of absorption, due to II, at 2020 cm.$^{-1}$ in the infrared. The ratio $[II]/[I]_0$ was plotted against time as is shown in Fig. 1. Such plots were used to estimate $[II]_{max}$ and t_{max}. Initial rates of formation of II were measured in experiments in which many measurements of [II] were made during the early parts of runs. Typical results are shown in Figs. 2 and 3. The data from these experiments are also included in Table I.

Decomposition of RR'.—The first-order rate constants for decomposition of the ketenimine were determined by following the disappearance of RR' by the infrared method. None of the other materials added or produced, such as α,α-diphenylpicryl-β-hydrazyl (DPPH), α,α-diphenyl-β-picrylhydrazine (HDPPH), 2,6-di-*t*-butyl-*p*-cresol or RR, absorb significantly at 2020 cm.$^{-1}$. Typical first-order plots of the data for decomposition of RR', with and without added scavengers, at 80 and 100° are shown in Figs. 4 and 5. The straight lines are those calculated by the method of least squares as are the values of the rate constants recorded in Table II. While most of the runs were carried out using individual, degassed, sealed ampoules, reasonably good agreement was also obtained by use of a batch-sampling technique described in the Experimental section. The rate constants used in calculations were obtained by averaging values obtained from runs which showed little scatter of points. The values were: without scavengers, 80.0°, 3.18×10^{-6} sec.$^{-1}$, 89.2°, 10.07×10^{-6} sec.$^{-1}$, and 100°, 40.45×10^{-6} sec.$^{-1}$; with DPPH at 80°, 4.99×10^{-6} sec.$^{-1}$; and with DPPH or oxygen plus DBPC at 100°, 66.17×10^{-6} sec.$^{-1}$. The rate of decomposition under oxygen was not determined at 80° since the reaction was so slow that significant loss of solvent occurred when oxygen was passed through

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[1] G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin and R. T. Keys, THIS JOURNAL, **82**, 5394 (1960).

[2] F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

[3] C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949).

[4] G. S. Hammond, O. D. Trapp, R. T. Keys and D. L. Neff, *ibid.*, **81**, 4878 (1959).

[5] C. Walling, private communication.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF 1,1'-AZOCYANOCYCLOHEXANE AND INITIAL RATE OF FORMATION OF N-(1-CYANOCYCLOHEXYL)-PENTAMETHYLENEKETENIMINE IN CHLOROBENZENE

$[RN_2R]_0 \times 10^2$, mole l.$^{-1}$	$[S]^a \times 10^2$, mole l.$^{-1}$	Temp., °C.	$k \times 10^6$, sec.$^{-1}$	$\frac{d[RR']/dt\ (t \rightarrow 0)^b}{[RN_2R]_0 k}$	$\frac{[RR']_{max}}{[RN_2R]_0}$	t_{max},^{e} hr.
3.92^c	....	79.97	8.425	0.69	0.377	52
3.98^c	....	79.97	8.416	.685	.374	52
13.26^f	....	79.7	8.25	...	...	
3.92^d	....	79.97	.....	.63	...	
7.82^d	....	79.97	.....	.66	...	
3.92^d	DPPH, 3.92	79.97	.....	.20	...	
7.81^d	DPPH, 3.92	79.97	.....	.206	...	
7.84^d	O_2 + DBPC, 7.80	79.97	.....	.21	...	
11.86^d	O_2 + DBPC, 7.82	79.92	.....	.218	...	
9.84^d	HDPPH, 4.10	79.92	.....	.226	...	
4.10^c	....	100.12	111.37	...	.36	4–4.2
5.04^c	....	100.12	110.07	.643	.374	4–4.2
8.26^c	....	100.12	.....	.649	...	..
4.10^d	....	100.12	.....	...	.37	4.2
11.83^c	DPPH, 4.08	100.12	.....	.17	...	..
11.55^d	O_2 + DBPC, 16.83	100.12	.....	.17	.075	2.25
11.67^c	HDPPH, 3.97	100.12	.....	.33	...	..
7.83^d	O_2	79.97	.....	0	...	....

[a] S is the scavenger; DPPH, α,α-diphenyl-β-picrylhydrazyl; DBPC, 2,6-di-*t*-butyl-*p*-cresol; HDPPH, α,α-diphenyl-β-picrylhydrazine. [b] Value for *k* used in the calculations is an average value; at 79.97°, 8.42×10^{-6} sec.$^{-1}$; at 100.12°, 110.72×10^{-6} sec.$^{-1}$. [c] Sealed-tube runs. [d] Batch-sampling. [e] Experimental values of t_{max}. [f] Monitoring nitrogen evolution.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF N-(1-CYANOCYCLOHEXYL)-PENTAMETHYLENEKETENIMINE IN CHLOROBENZENE

$[RR']_0 \times 10^2$, mole l.$^{-1}$	$[S]^a \times 10^2$, mole l.$^{-1}$	Temp., °C.	$k \times 10^6$, sec.$^{-1}$
1.19^c	....	79.97	3.20
1.57^c	....	79.97	3.16
0.80^{b,c}	....	79.97	3.39
1.20^c	....	89.20	10.07
1.19^c	DPPH, 2.45	79.97	5.00
1.57^c	DPPH, 3.24	79.97	4.98
0.80^{c,b}	HDPPH, 1.82	79.97	6.65
1.19^c	HDPPH, 2.36	79.97	6.17
1.18^c	HDPPH, 3.63	79.97	6.36
1.21^d	....	100.12	41.09
1.62^c	....	100.12	39.82
1.64^c	DPPH, 3.24	100.12	66.24
1.40^d	O_2 + DBPC, 4.38	100.12	66.10
1.65^c	HDPPH, 3.24	100.12	75.14
1.20^d	O_2	100.12	145.40
1.48^d	O_2	100.12	143.30

[a] S is the radical scavenger; see footnote to Table I. [b] Points scatter somewhat. [c] Sealed-tube technique. [d] Batch-sampling technique.

the solution for the period required to make a run. Still higher decomposition rates were observed in the presence of HDPPH or under oxygen with no antioxidant present.

Efficiencies of Radical Production from RN_2R and RR'.—Two methods were used to measure the rates of radical production from RN_2R. Table III shows the results obtained by measurement of the length of the induction periods produced by DBPC in the oxidation of cumene initiated by various amounts of RN_2R in 2:1 (by volume) chlorobenzene–cumene mixture. Complete details of the method, including assignment of stoichiometric factors for antioxidants, have been discussed in detail earlier.[6] The results are reported in terms of *a*, the efficiency of radical production in the decomposition of RN_2R. The efficiency factors were calculated from the equation

$$a = 2[DBPC]_0/[RN_2R]_0 2kt_l,$$

in which *k* is the rate constant for decomposition of RN_2R, 2 is radical-stopping capacity of DBPC, and t_l is the inhibition period. The relationship is valid as long as $kt_l << 1$. At 80° this last condition is easily fulfilled by adjustment of the concentrations of the initiator and the antioxidant. Table IV gives the results of measurements of *a* by

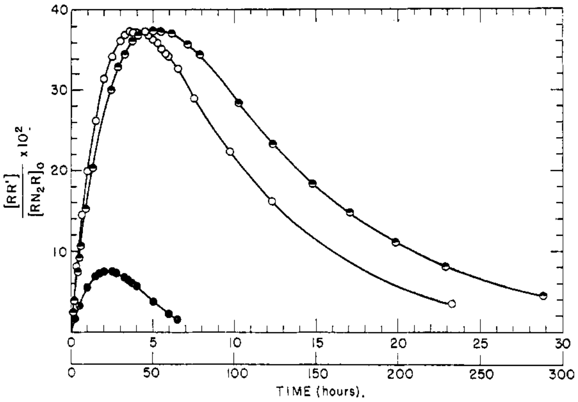

Fig. 1.—Formation of N-(1-cyanocyclohexyl)-pentamethyleneketenimine by decomposition of 1,1'-azacyanocyclohexane in chlorobenzene: ◓, $[RN_2R]_0 = 3.98 \times 10^{-2}$ mole l.$^{-1}$ at 80°, lower abscissa scale; O, $[RN_2R]_0 = 5.04 \times 10^{-2}$ mole l.$^{-1}$ at 100°, upper abscissa scale; ●, $[RN_2R]_0 = 11.55 \times 10^{-2}$ mole l.$^{-1}$ at 100°, under oxygen, $[DBPC]_0 = 16.83 \times 10^{-2}$ mole l.$^{-1}$, upper abscissa scale.

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[6] C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, THIS JOURNAL, **77**, 3234 (1955).

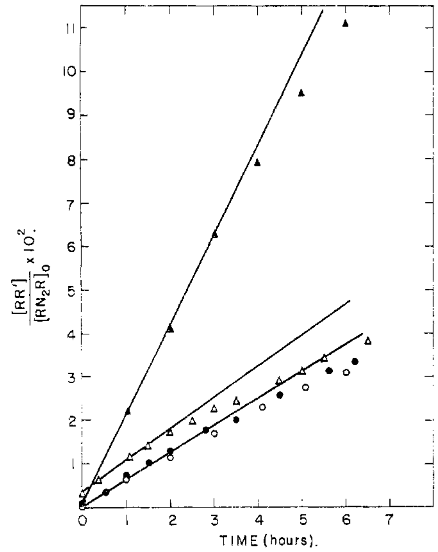

Fig. 2.—Initial rate of formation of N-(1-cyanocyclohexyl)-pentamethyleneketenimine by decomposition of 1,1'-azocyanocyclohexane in chlorobenzene at 80°: ▲, $[RN_2R]_0 = 3.92 \times 10^{-2}$ mole l.$^{-1}$; △, $[RN_2R]_0 = 9.84 \times 10^{-2}$ mole l.$^{-1}$, $[HDPPH]_0 = 4.10 \times 10^{-2}$ mole l.$^{-1}$; ○, $[RN_2R]_0 = 7.81 \times 10^{-2}$ mole l.$^{-1}$, $[DPPH]_0 = 3.92 \times 10^{-2}$ mole l.$^{-1}$; ●, $[RN_2R]_0 = 7.84 \times 10^{-2}$ mole l.$^{-1}$, under oxygen, $[DBPC]_0 = 7.80 \times 10^{-2}$ mole l.$^{-1}$.

the iodine-lifetime method.[7] Values of a at 80° were calculated from the equation

$$a = [I_2]_0/[RN_2R]_0kt_l.$$

At 100° it was not possible to fulfill the condition $kt_l << 1$ and still make t_l long enough for accurate measurement. The plots of iodine concentration against time showed noticeable curvature because the decay of RN_2R was significant over the course of an experiment. In such runs the a factor was calculated either using the appropriate exponential expression for the concentration of the azo compound

$$a = [I_2]_0/[RN_2R]_0(1 - e^{-kt_l})$$

or by careful measurement of a tangent to the curve at time zero

$$a = -(d[I_2]/dt)_{t\rightarrow 0}/[RN_2R]_0k$$

TABLE III

EFFICIENCY OF RADICAL PRODUCTION OF 1,1'-AZOCYANOCYCLOHEXANE AND N-(1-CYANOCYCLOHEXYL)-PENTAMETHYLENEKETENIMINE IN CHLOROBENZENE DETERMINED BY INHIBITION PERIOD OF OXIDATION MEASUREMENT

$[RN_2R]_0\cdot10^2$ or $[RR']_0 \times 10^2$, mole l.$^{-1}$	$[DBPC]_0 \times 10^2$, mole l.$^{-1}$	Temp., °C.	Inhibition period, min.	Efficiency a	a'	$-\frac{dO_2}{dt}$[a], ml. min.$^{-1}$
16.78	0.167	79.7	33.0	0.61[b]		0.124
8.32	.168	79.7	68.5	.60[b]		.086
12.5	.168	79.7	45.7	.60[b]		.104
8.24	.168	79.97	65.5	.62[c]		.088
8.3	.084	79.7	80.0		0.424[d]	.056
8.3	.084	79.7	79.5		0.43[d]	.056

[a] Steady rate of oxidation after the inhibition period. [b] Value of k was assumed to be 8.25×10^{-6} sec.$^{-1}$ [c] Value of k was assumed to be 8.42×10^{-6} sec.$^{-1}$. [d] Value assumed for rate constant for decomposition of RR' was 4.99×10^{-6} sec.$^{-1}$.

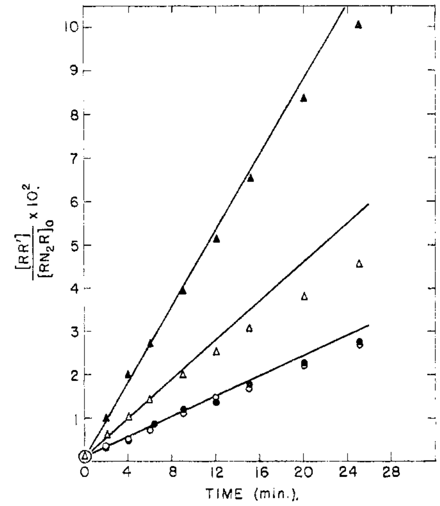

Fig. 3.—Initial rate of formation of N-(1-cyanocyclohexyl)-pentamethyleneketenimine by decomposition of 1,1'-azocyanocyclohexane in chlorobenzene at 100°: ▲, $[RN_2R]_0 = 8.26 \times 10^{-2}$ mole l.$^{-1}$; △, $[RN_2R]_0 = 11.67 \times 10^{-2}$ mole l.$^{-1}$, $[HDPPH]_0 = 3.97 \times 10^{-2}$ mole l.$^{-1}$; ○, $[RN_2R]_0 = 11.83 \times 10^{-2}$ mole l.$^{-1}$, $[DPPH]_0 = 4.08 \times 10^{-2}$ mole l.$^{-1}$; ●, $[RN_2R]_0 = 11.55 \times 10^{-2}$ mole l.$^{-1}$, under oxygen, $[DBPC]_0 = 16.83 \times 10^{-2}$ mole l.$^{-1}$.

Since iodine catalyzes rapid destruction of RR', the iodine-lifetime method cannot be used to measure the rate of radical production from the ketenimine. The oxidation-inhibition method is applicable and has been used. The results are included in Table III, expressed in terms of a', which is calculated using the rate of decomposition of RR' *in the presence of scavengers.*

TABLE IV

EFFICIENCY OF RADICAL PRODUCTION OF 1,1'-AZOCYANOCYCLOHEXANE IN CHLOROBENZENE DETERMINED BY IODINE-LIFETIME MEASUREMENT

$[RN_2R]_0 \times 10^2$, mole l.$^{-1}$	$[I_2]_0 \times 10^2$, mole l.$^{-1}$	Temp., °C.	Time, min.	Efficiency, a
6.004[a]	0.169	79.97	82.4	0.676[c]
5.982[a]	.107	79.97	52.6	.671[c]
5.988[a]	.081	79.97	39.8	.669[c]
0.70[b]	.091	100.12	31	.697[d](0.697[e])
0.70[b]	.075	100.12	25	.696[d](0.691[e])

[a] Batch-sampling technique. [b] Sealed-tube experiments. [c] Calculated from $a = [I_2]_0/[RN_2R]_0kt_l$; $k = 8.42 \times 10^{-6}$ sec.$^{-1}$. [d] Calculated from $a = [I_2]_0/[RN_2R]_0(1-e^{-kt_l})$; $k = 110.7 \times 10^{-6}$ sec.$^{-1}$. [e] Calculated from $a = -(d[I_2]/dt)_{t\rightarrow 0}/k[RN_2R]_0$; $k = 110.7 \times 10^{-6}$ sec.$^{-1}$

An additional method is available for measurement of the efficiency of RR' relative to that of RN_2R. The rate of uninhibited oxidation is given by the equation

$$R_0 = \frac{(2ak[\text{initiator}])^{1/2}k_p[RH]}{k_t^{1/2}} + 2ak[\text{initiator}]$$

$$\cong \frac{(2ak[\text{initiator}])^{1/2}k_p[RH]}{k_t^{1/2}}$$

R_0 is the rate of oxygen uptake; k_p is the rate constant for the chain propagating reaction, $RO_2\cdot$ +

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[7] G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, 77 3244 (1955).

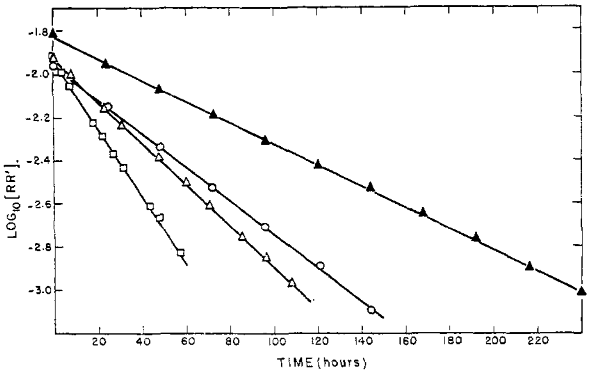

Fig. 4.—Decomposition of N-(1-cyanocyclohexyl)-pentamethyleneketenimine in chlorobenzene at 80° and 89.2°: ▲, $[RR']_0 = 1.57 \times 10^{-2}$ mole l.$^{-1}$ at 80°; O, $[RR']_0 = 1.19 \times 10^{-2}$ mole l.$^{-1}$, $[DPPH]_0 = 2.45 \times 10^{-2}$ mole l.$^{-1}$ at 80°; △, $[RR']_0 = 1.19 \times 10^{-2}$ mole l.$^{-1}$, $[HDPPH]_0 = 2.36 \times 10^{-2}$ mole l.$^{-1}$ at 80°; □, $[RR']_0 = 1.20 \times 10^{-2}$ mole l.$^{-1}$ at 89.2°.

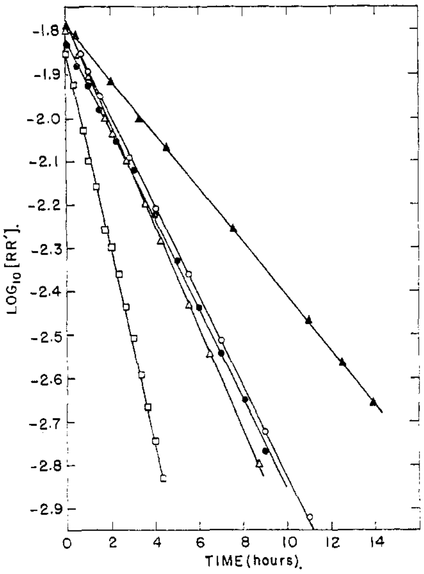

Fig. 5.—Decomposition of N-(1-cyanocyclohexyl)-pentamethyleneketenimine in chlorobenzene at 100°: ▲, $[RR']_0 = 1.62 \times 10^{-2}$ mole l.$^{-1}$; O, $[RR']_0 = 1.64 \times 10^{-2}$ mole l.$^{-1}$, $[DPPH]_0 = 3.24 \times 10^{-2}$ mole l.$^{-1}$; ●, $[RR']_0 = 1.49 \times 10^{-2}$ mole l.$^{-1}$, under oxygen, $[DBPC]_0 = 4.38 \times 10^{-2}$ mole l.$^{-1}$; △, $[RR']_0 = 1.65 \times 10^{-2}$ mole l.$^{-1}$, $[HDPPH]_0 = 3.24 \times 10^{-2}$ mole l.$^{-1}$; □, $[RR']_0 = 1.48 \times 10^{-2}$ mole l.$^{-1}$, under oxygen.

$RH \rightarrow RO_2H + R\cdot$; and k_t is the rate constant for chain termination by reaction of two $RO_2\cdot$ radicals with each other. The second term of the equation represents oxygen consumed directly by initiator fragments and is negligible in comparison with the first term in our experiments. Rates of cumene oxidation initiated by RR' and RN_2R were measured under conditions which were identical except for the nature of the initiator. From the rate ratios it is possible to calculate directly the ratios of the terms ak for the two initiators.

$$\frac{R_0{}^2{}_{(RN_2R)}}{R_0{}^2{}_{(RR')}} = \frac{ak[RN_2R]}{a'k'[RR']}$$

Table V contains a summary of data for oxidation rates and the ratio a/a', calculated assuming that k' is the rate constant for RR' decomposition in the presence of scavengers.

TABLE V

THE CALCULATED a/a' AT 80° FROM THE RATES OF OXIDATION OF CUMENE WITH RN_2R AND RR' AS INITATOR

$[RN_2R] \times 10^2$, mole l.$^{-1}$	$(-dO_2/dt)_{RN_2R}$	$k_{RN_2R} \times 10^6$, sec.$^{-1}$	$[RR'] \times 10^2$, mole l.$^{-1}$	$(-dO_2/dt)_{RR'}$	$k_{RR'} \times 10^5$, sec.$^{-1}$	a^a/a'
16.51	0.124	8.25	8.10	0.0559	4.99	1.4347
8.04	.086	8.25	8.10	.0559	4.99	1.3980
12.22	.104	8.25	8.10	.0559	4.99	1.4496
7.97	.088	8.42	8.10	.0559	4.99	1.4920

[a] The average of the four a/a' values is 1.4415.

Neither oxidative procedure can be used with our present equipment at 100°; therefore, we do not at this time have a suitable procedure for measuring the efficiency of RR' at the higher temperature.

Discussion

Mechanism of the Decompositions.—The following equations describe the decomposition of an azonitrile and the related ketenimine if it is assumed that inefficiency is due to coupling of radicals before they are separated by diffusion from the solvent cage. The only reactions of cyanoalkyl radicals which are considered explicitly are coupling to give RR and RR'. Disproportionation[8] will also give a small amount of additional, inert products which in this analysis are counted as RR.

$$RN_2R \xrightarrow{k_1} \overline{2R\cdot + N_2} \; (R\cdot = {>}\dot{C}{-}CN \leftrightarrow {>}C{=}C{=}N\,) \tag{1}$$

$$\overline{2R\cdot + N_2} \xrightarrow{k_2'} RR + \text{disproportionation} + N_2 \tag{2}$$

$$\overline{2R\cdot + N_2} \xrightarrow{k_3'} RR' + N_2 \tag{3}$$

$$\overline{2R\cdot + N_2} \xrightarrow{k_4} \underset{\text{"free" radicals}}{2R\cdot + N_2} \tag{4}$$

$$2R\cdot \xrightarrow{k_2} RR \tag{5}$$

$$2R\cdot \xrightarrow{k_3} RR' \tag{6}$$

$$RR' \xrightarrow{k_1'} \overline{2R\cdot} \tag{7}$$

$$\overline{2R\cdot} \xrightarrow{k_2''} RR \tag{8}$$

$$\overline{2R\cdot} \xrightarrow{k_3''} RR' \tag{9}$$

$$\overline{2R\cdot} \xrightarrow{k_4'} 2R\cdot \tag{10}$$

Pairs of radicals which have not been separated by diffusion are indicated by placing a bar over the formulas. Inclusion of the nitrogen molecule as a part of the associated group formed by decomposition of the azo compound is important since it probably separates the radicals by one molecular diameter at the moment of their formation. The radicals which escape from the cage without undergoing primary coupling reactions will surely achieve complete thermal equilibrium. Therefore, no distinction is made between the "free" radicals produced from RR' and those produced from RN_2R.

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(8) A. F. Bickel and W. A. Waters, *Rec. trav chim* 1490 (1950).

Fraction of the Decomposition of RN_2R Leading to Formation of RR′ Inside and Outside the Cage.—The rate law for formation of RR′ from RN_2R in the absence of scavengers is given by eq. 11.

$$d[RR']/dt = zk_1[RN_2R] - yk_1'[RR'] = zk_1[RN_2R]_0e^{-k_1t} - yk_1'[RR']$$

$$z = \underset{\text{(in the cage)}}{\frac{k_3'}{k_2' + k_3' + k_4}} + \underset{\text{(outside the cage)}}{\frac{k_3k_4}{(k_2 + k_3)(k_2' + k_3' + k_4)}}$$

$$y = 1 - \left\{\frac{k_3''}{k_2'' + k_3'' + k_4'} + \frac{k_3k_4'}{(k_2 + k_3)(k_2'' + k_3'' + k_4')}\right\} \quad (11)$$

Experimentally, yk_1' is the first-order rate constant for decomposition of RR′ in the absence of scavengers. Since RR′ is zero at the start of a run, the initial rate of formation of RR′ gives z directly (see Figs. 2 and 3).

$$(d[RR']/dt)_{t \to 0} = zk_1[RN_2R]_0 \quad (12)$$

The value of z may also be determined by measuring the maximum concentration of RR′ and the time at which this maximum is reached. Integration of eq. 11 gives eq. 13

$$\frac{[RR']}{[RN_2R]_0} = \frac{zk_1}{k_1 - yk_1'}(e^{-k_1't} - e^{-k_1t}) \quad (13)$$

At t_{max}, $d[RR']/dt = 0$

$$[RR']_{max}/[RN_2R]_0 = zK^{K/1-K} \quad (14)$$

$$t_{max}\,k_1 = \frac{1}{K - 1}\ln K \quad (15)$$

where $K = yk_1'/k_1$.

The values of $[RR']/[RN_2R]_0$ are plotted as a function of time in Fig. 1. The curve is qualitatively similar to that describing the formation of N-[2-cyano-2-propyl]-dimethylketenimine from ABN.[1,9] The data required for calculation of z-values are included in Table I, and a comparison of the values as calculated by the two methods are presented in Table VI. At 80°, 69% of the azo compound is converted to ketenimine and at 100° the value is 65%.

TABLE VI

COMPARISON OF z-VALUES DETERMINED BY MEASUREMENT OF INITIAL RATES OF RR′ FORMATION AND FROM LOCATION OF $[RR']_{max}$

T, °C.	$[RN_2R]_{max}/[RN_2R]_0$	K	t_{max}, hr.	z
79.97	0.375	0.378	52,[a] 51.6[b]	0.69,[c] 0.68[d]
100.12	0.374	0.365	4.0–4.2,[a] 3.98[b]	0.645,[c] 0.66[d]

[a] Experimental value. [b] Value calculated from eq. 15. [c] From initial slope. [d] Value calculated from eq. 14.

When RN_2R is decomposed in the presence of scavengers such as DPPH or oxygen and an antioxidant, the "free" radicals are intercepted and reaction 16 replaces reactions 5 and 6

$$R\cdot + S \xrightarrow{k_{16}} \text{stable products} \quad (16)$$

The assumption that k_{16}, for any particular scavenger, is sufficiently large to completely inhibit the radical coupling reactions is easily checked by ascertaining that the initial rate of formation of RR′ from RN_2R is independent of the concentration of the scavenger.

$$z' = \frac{(d[RR']/dt)_S + y'k_1'[RR']}{k_1[RN_2R]} = \frac{k_3'}{k_2' + k_3' + k_4} \quad (17)$$

Measurements of the initial rates of formation of RR′ from RN_2R in the presence of oxygen plus DBPC or DPPH give z'-values of 0.21 at 80° and 0.17 at 100°. The alternative method of measurement, using $[RR']_{max}$, cannot be conveniently used at 80° (see previous section), but the formation of RR′ was studied in detail in the presence of oxygen and DBPC at 100°. Table VII compares the values of z' and t_{max}. The latter do not check as well as would be expected with calculated values of t_{max} for reasons which we cannot explain.

TABLE VII

VALUES OF z' AND t_{max} FROM THE DECOMPOSITION OF RN_2R IN THE PRESENCE OF SCAVENGERS

T, °C.	$[RR]_{max}/[RN_2R]_0$	K	t_{max}, hr.	z'
79.97	....	0.593	....	0.21[d]
100.12	0.075[a]	0.597	2.25,[b] 3.2[c]	0.17,[d] 0.16[e]

[a] Oxygen plus DBPC. [b] Experimental value. [c] Calculated from eq. 15. [d] Initial rate. [e] Calculated from eq. 14.

Acceleration of the Rate of Decomposition of RR′ by Radical Scavengers.—Equations 18 and 19 give expressions for V, the rate of ketenimine decomposition in the absence of scavengers and for V_s, the rate of decomposition in the presence of scavengers.

$$V = -d[RR']/dt = yk_1'[RR'] \quad (18)$$

$$y = 1 - \left\{\frac{k_3''}{k_2'' + k_3'' + k_4'} + \frac{k_3k_4'}{(k_2 + k_3)(k_2'' + k_3'' + k_4')}\right\}$$

$$V_s = -(d[RR']/dt)_s = y'k_1'[RR'] \quad (19)$$

$$y' = 1 - \frac{k_3''}{k_2'' + k_3'' + k_4'}$$

The more rapid decomposition in the presence of scavengers is due to the disappearance of reaction 6, the coupling of "free" radicals to regenerate RR′. If the scavenging reaction is completely efficient, the rate should be independent of the scavenger concentration as long as any is left in the solution. The results shown in Table II are in full accord with the hypothesis.

It is significant that the ratio V/V_s is essentially the same at 80° and at 100°. They are: $(V/V_s)_{80°} = 0.636$ and $(V/V_s)_{100°} = 0.61$. By dividing eq. 18 by eq. 19 we obtain 20.

$$y/y' = 1 - \frac{k_4'}{k_2'' + k_4'} \times \frac{k_3}{k_2 + k_3} \quad (20)$$

The fact that y/y' is nearly temperature independent implies that the competitive reactions have very similar activation energies. This, in turn, is most likely to be true if all of the reactions have low activation energies, as would be expected of the coupling and diffusion of radicals.

Efficiency of Production of "Free" Radicals from RN_2R and RR′.—The factor a is the fraction of the total number of RN_2R decompositions which yields kinetically free radicals. The values of a for

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(9) M. Talât-Erben and S. Bywater, THIS JOURNAL, **77**, 3710, 3712 (1955).

ABN measured by the oxidation-inhibition method and by the iodine-lifetime method agreed rather well in a number of solvents, although the values obtained by oxidation inhibition were always slightly smaller than those obtained in iodine scavenging experiments.[7] In this investigation the *a* factor measured by the oxidation procedure is lower than that estimated by iodine by an amount which is larger than the combined experimental imprecision of the methods. Two explanations for this fact come to mind. First, the efficiency factors may actually be different because the solvent is different in the two experiments since about 33% cumene is present in the oxidation studies. There may be reason to believe that cumene, an electron-rich aromatic molecule, may form complexes with cyanoalkyl radicals, thereby reducing the magnitude of the cage effect. Alternatively, it is possible that one or the other of the scavenging reactions deviates from the assumed stoichiometry. If a stoichiometric deviation is involved, it is most likely to be involved in the experiments with iodine. Some ketenimine is formed from RN_2R in the presence of DPPH, HDPPH or oxygen and an antioxidant. Therefore it may be presumed that some is also formed in the presence of iodine. However, spectroscopic analysis shows that it never accumulates to measurable concentration. We have found that small amounts of iodine destroy relatively large amounts of ketenimine. This destruction is known to be, at least in part, catalytic but we do not know that *no* iodine is consumed in the process. If a small amount of iodine is used up in destruction of RR', this will increase the rate of iodine loss and will give a spuriously high value of *a*. Although we favor the latter explanation, we have no rigorous means of deciding between the two at this time. For this reason, both values of *a* are reported in Tables III and IV and used in subsequent calculations.

Only the oxidation inhibition is applicable for determination of the efficiency factor, *a'*, for RR'. Equations 21 and 22 translate this factor in terms of the rate constants for equations 7 to 10.

$$-\frac{d[S]}{dt} = \frac{d[R\cdot]}{n dt} = \frac{2k_1'[RR']}{n}\left\{1 - \frac{k_3''}{k_2'' + k_3'' + k_4'}\right\}\frac{k_4'}{k_2'' + k_4'} \qquad (21)$$

$$\left(n = 2 \text{ for DBPC and } k_1'\left\{1 - \frac{k_3''}{k_2'' + k_3'' + k_4'}\right\} = y'k_1'\right)$$

$$\frac{d[S]}{d[RR']_{\text{scavenged}}} = \frac{k_4'}{k_2'' + k_4'} = a' \qquad (22)$$

It is noteworthy that *a'* does not measure the total cage effect in the decomposition of RR' since no account is taken of those radical pairs which regenerate RR' by primary recombination.

The Characteristic Ratios ($k_3/k_2 + k_3$) and ($k_3'/k_2' + k_3'$).—Since k_2, k_3, k_2' and k_3' are the rate constants for corresponding coupling reactions in primary and secondary recombination, comparison of these quantities is probably the surest way of establishing the character of the "cage reactions." There are two ways of obtaining $k_3/k_2 + k_3$: (1) from the rates of formation of RR' from RN_2R; subtracting eq. 17 from eq. 11 gives eq. 23.

$$z - z' = \frac{ak_3}{k_2 + k_3} \qquad (23)$$

Values of $k_3/k_2 + k_3$ at 80° have been calculated using both values of *a* (see previous section). (2) From the rates of decomposition of RR'; combining eq. 20 and 22 gives eq. 24

$$\frac{y}{y'} = 1 - \frac{a'k_3}{k_2 + k_3} \qquad (24)$$

Table VIII shows the values of $k_3/k_2 + k_3$ obtained by the various calculations. The value obtained from data for rates of ketenimine decomposition agrees well with that obtained using the lower value of *a* for RN_2R. However, this fact cannot justifiably be used to choose between the *a*-values since oxygen scavenging was used in the determination of the value of *a'* for the ketenimine. If there is a fault in the assumptions made concerning oxygen scavenging it will likely be reflected in both *a* and *a'*.

TABLE VIII

VALUES OF ($k_3/k_2 + k_3$) AND ($k_3'/k_2' + k_3'$)

Source of the value	$k_3/k_2 + k_3$	$k_3'/k_2' + k_3'$
Decompn. of RN_2R at 80° (*a* (*a* = 0.61)	0.79	0.54
Decompn. of RN_2R at 80° (*a* (*a* = 0.67)	.72	.64
Decompn. of RN_2R at 100°	.68	.57
Decompn. of RR' at 80°	.84	..

The value of $k_3'/k_2' + k_3'$ may be obtained from eq. 25 involving the yield of RR' from RN_2R in the presence of scavengers and the efficiency, *a*, of radical production from RN_2R.

$$\frac{z'}{1 - a} = \frac{k_3'}{k_2' + k_3'} \qquad (25)$$

The values of $k_3'/k_2' + k_3'$ derived from the two values of *a* are entered in Table VIII. It is certain that if the value of *a* obtained from oxidation data is correct, the value of $k_3'/k_2' + k_3'$ is significantly different from the value of $k_3/k_2 + k_3$. If the value of *a* from iodine-lifetime measurements is correct, it is possible, but not likely, that the true values of the two ratios are the same. These data will be discussed in greater detail in the second paper.

Activation Parameters.—Activation energies and enthalpies and entropies of activation for the decomposition of RN_2R and RR' are summarized in Table IX. Our value of E_{act} is smaller than that reported by Lewis and Matheson[2] and slightly smaller than the figure reported by Overberger.[10]

TABLE IX

ACTIVATION PARAMETERS

Function[a]	RN_2R	RR' No scavenger	RR' DPPH	RR' HDPPH
E_{act}	33.5	33.2	33.6	32.3
ΔH^*	32.8	32.5	32.9	31.6
ΔS^*	10.8	8.0	10.0	6.7

[a] Units: E_{act} and ΔH^*, kcal. mole^{-1}; ΔS^*, cal. mole^{-1} deg.$^{-1}$.

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[10] C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker and J. Herbert, THIS JOURNAL, **75**, 2078 (1953).

Several Interesting but Still Ambiguous Aspects of the Study.—α,α-Diphenyl-β-picrylhydrazine (HDPPH) and oxygen *without any added antioxidant* give anomalous behavior as scavengers. Both accelerate the decomposition of RR′ more than DPPH or oxygen *with an antioxidant*. Since addition of an antioxidant reduces the rate in the presence of oxygen to that observed with DPPH, it is clearly indicated that $RO_2\cdot$ must react with RR′. The same indication is provided by the fact that no detectable amount of RR′ is formed when RN_2R is decomposed under an atmosphere of oxygen with no added antioxidant.

The behavior of HDPPH is probably attributable to some similar phenomenon. Some radical, probably R·, must react with the hydrazine to give a radical, not DPPH, which in turn reacts rapidly with the ketenimine. When RN_2R is decomposed in the presence of HDPPH at 80° the formation of RR′ is retarded by about the same amount as in experiments using DPPH as a scavenger. The retardation is less at 100°. The latter fact simply indicates that HDPPH is not a completely efficient scavenger. If this is the case, the effects on the rate of ketenimine production at 80° may represent a mixture of partially efficient radical scavenging action and induced decomposition of RR′.

A further, thought-provoking observation is the iodine-catalyzed destruction of ketenimine. Very rapid disappearance of RR′ was observed, even at room temperature, when iodine was added to solutions of RR′ in chlorobenzene. Catalytic action was indicated by the fact that relatively small amounts of iodine were required to effect essentially complete destruction of RR′.

Bromine, as might have been expected, is consumed at an unreliably rapid rate when it is added to ABN decomposition mixtures. The effect of the compound was studied since it should be an effective scavenger for ketenimine as well as "free" radicals. However, the rate of disappearance of bromine ranged from 97 to 156% of the rate of RN_2R decomposition, clearly indicating the occurrence of some addition reaction. The bromine lifetimes were erratic in addition to being shorter than anticipated. The data are summarized in Table X.

TABLE X

SCAVENGING OF RADICAL AND KETENIMINE PRODUCED BY 1,1′-AZOCYANOCYCLOHEXANE IN CHLOROBENZENE AT 80°[a]

Run	$[RN_2R]_0$, mole l.$^{-1}$	$[Br_2]_0$, mole l.$^{-1}$ $\times 10^{-3}$	Temp., °C.	Lifetime of Br_2, min.	b[b]
2	0.100	3.28	79.97	66.0	0.973
3	.100	4.50	79.97	85.5	1.045
4	.100	2.87	79.97	48.0	1.186
5	.100	2.48	79.97	35.0	1.407
6	.100	3.59	79.97	58.3	1.221
7	.100	3.05	79.97	38.8	1.56
8	.100	4.26	79.97	70.0	1.209

[a] Batch-sampling, run under nitrogen. [b] $b = [Br_2]_0/[RN_2R]_0kt_1$.

Experimental

Commercial Materials.—The **bromine** employed in this work was J. T. Baker Analyzed reagent grade and was used without further purification. **Carbon tetrachloride**, Baker and Adamson reagent grade, was redistilled before use. **Iodine**, Baker and Adamson reagent grade, was resublimed twice. **Chlorobenzene**, Matheson, Coleman and Bell white label grade, was purified by extraction with small portions of concentrated sulfuric acid; washed successively with distilled water, 5% aqueous sodium bicarbonate solution, and again with distilled water; dried with anhydrous magnesium sulfate and Drierite; and, finally, distilled from phosphorus pentoxide through a 30-in. vacuum-jacketed column containing randomly packed metal helices. The fraction boiling at 130° (740 mm.)[11] was used in kinetic studies. **2,6-Di-*t*-butyl-*p*-cresol**, Eastman Kodak yellow label grade, was purified by two recrystallizations from ethanol, m.p. 70°.

α,α-Diphenyl-β-picrylhydrazine (HDPPH) was prepared by the method of Poirier, Kahler and Benington[12]; m.p. 168–169°.

α,α-Diphenyl-β-picrylhydrazyl (DPPH) was prepared by oxidation of the hydrazine by the method of Goldschmidt and Renn.[13] Three recrystallizations of the crude material from chloroform and anhydrous ethyl ether (1:2) by volume gave material melting 136–7° (lit.[14] 137°).

1,1′-Azocyanocyclohexane (RN_2R).—The method of Overberger[3] was used to prepare RNHNHR in quantitative yield. To one mole of RNHNHR was added two moles of 2 *N* hydrochloric acid. The mixture was stirred efficiently at room temperature and bromine was added to the slurry at a moderate rate until a permanent, yellow color was obtained. The product was recrystallized three times from methanol giving RN_2R, m.p. 113–4° dec. (lit.[10] 114–5° dec.); ϵ at 3500 Å. 17.9 l. mole^{-1} cm.$^{-1}$ in ethanol and 19.4 l. mole^{-1} cm.$^{-1}$ in chlorobenzene (lit.[15] ϵ at 3500 Å. in ethanol, 17 l. mole^{-1} cm.$^{-1}$).

N-(1-Cyanocyclohexyl)-pentamethyleneketenimine (RR′).—Heptane (one l.) and RN_2R (155 g.) were placed in a 2-liter, three-necked, round-bottom flask fitted with a mechanical stirrer, reflux condenser, thermometer and nitrogen bubbler. Nitrogen gas, purified by passage through two gas-washing towers containing pyrogallol solution[16] and a tower of Drierite, was purged through the mixture at room temperature for 40 minutes. The mixture was heated to the reflux temperature over the course of 20 minutes, maintained at the reflux temperature for 12 hours, and then cooled to room temperature over the course of an hour. During the course of the reaction, nitrogen was bubbled through the reaction mixture at a moderate rate. A U-tube filled with mineral oil was attached to the exit end of the condenser to serve as a pressure gauge to regulate the gas flow and to exclude air from the reaction system. The reaction mixture was allowed to stand overnight and then the crystalline precipitate was removed by filtration through a büchner funnel. The solid, approximately 75 g., m.p. 218–220°, was essentially pure 1,1′-dicyanobicyclohexyl (RR) (lit.[9] m.p. 224–225°). The filtrate was cooled to 5° and yielded an additional 3.3 g. of solid, m.p. 98–170°, which gave only a negligible amount of sublimate when heated at 31° under 2 mm. pressure. This material was probably a mixture of RR and unreacted RN_2R. The filtrate was concentrated to 200 ml. by rapid distillation at room temperature under 20 mm. pressure. The distillate left no residue when allowed to evaporate at room temperature. The residual liquid was cooled to 5° and a precipitate separated, 30 g., m.p. 60–68° (fraction 1). The filtrate was again concentrated, and chilling gave an additional 13.3 g., m.p. 54–66° (fraction 2). The remaining liquid was then allowed to evaporate in an open dish at room temperature, yielding 7–8 g. of tacky, yellow residue (fraction 3). Fractions 1 and 2 contained chiefly RR′, and fraction 3 contained a significant amount of the material. Purification of crude RR′ was achieved by multiple sublimation at 29° and 2–4 mm., a procedure in which little loss was suffered. Fractional recrystallization from hydrocarbon solvents also accomplished good purification, but with higher losses. Attempts at purification by column chromatography were unsuccessful because RR′ decomposed on silicic acid, Celite or acid-washed alumina with the formation of an unknown compound, m.p. 150°.

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[11] All melting and boiling points are uncorrected.

[12] R. H. Poirier, E. J. Kahler and F. Benington, *J. Org. Chem.*, **17**, 1437 (1952).

[13] S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

[14] J. A. Lyons and W. F. Watson, *J. Polymer Sci.*, **18**, 141 (1955).

[15] H. W. Melville and S. Richards, *J. Chem. Soc.*, 944 (1954).

[16] C. R. N. Strouts, J. H. Gilfillan and H. N. Wilson, "Analytical Chemistry," Vol. I, The Clarendon Press, London, 1955, p. 449.

Adsorbents such as calcium carbonate and calcium hydroxide neither purified nor decomposed RR'. Aluminum oxide (Merck reagent, ignited, lot no. 71701) did not absorb RR' appreciably and removed impurities effectively in a chromatographic filtration. Such a treatment was equivalent to at least one sublimation. Pure RR' melted at 68-69°; ϵ at 2020 cm.$^{-1}$, 456 l. mole^{-1} cm.$^{-1}$ in carbon tetrachloride; assay by bromine titration in carbon tetrachloride,[4] 101 ± 1%. Dr. Rivin[5] has compared a sample of our material with that which he had prepared and found the substances to be essentially identical. *Anal.* Calcd. for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95. Found: C, 77.68; H, 9.30; N, 13.04.[17]

Kinetic Methods. Batch-sampling.—The reaction vessel was made by modification of a 300-ml. Kjeldahl flask. The pear-shaped chamber was elongated to a narrow column, the top part of the column was converted to a water condenser, and a ground female joint was sealed to the end. A three-way stopcock was sealed to a matching male joint. One outlet from the cock was vented to the atmosphere through a U-tube bubbler which was filled with glycerol or mineral oil. Three fixtures were added to the chamber; a glass thermometer well; a short side arm of suitable diameter to accept a rubber serum stopper with a snug fit; and a glass inlet tube which led, through a three-way stopcock, to the bottom of the chamber. The inlet tube was supported by a reinforcement fused to the side of the vessel.

If the reaction was to be conducted under nitrogen, the gas was purified by passage through pyrogallol solution, Drierite and two gas-washing towers containing chlorobenzene (to presaturate the gas with solvent). The gas was passed through the flask for 10 minutes before the reaction was started. The reaction mixture was then prepared by mixing appropriate amounts of reagents and solvent in a volumetric flask (50 or 100 ml.). The solution was poured into the reaction vessel through the small side arm and the latter was then closed with a serum stopper. With water circulating through the condenser, nitrogen was passed through the mixture at a moderate rate for about 1 hour. The change in concentration caused by this deoxygenation procedure was shown to be negligible by measurement of the absorbence of the solution at 3700 Å. before and after flushing. Then the speed of the nitrogen stream was reduced to a very slow rate and the reaction vessel was dipped into the constant temperature bath to a depth sufficient to completely submerge the reaction chamber. For the first 3 minutes the vessel was shaken manually; 5 minutes after immersion was taken as zero time for the reaction and a sample was withdrawn and analyzed spectrophotometrically to establish concentration conditions at zero time. Samples were withdrawn by means of a hypodermic syringe inserted through the serum stopper. Samples were delivered into test-tubes fitted with ground-glass stoppers and the tubes were cooled in ice-water. The stoppered tubes were shaken vigorously to speed the quenching by cooling. Samples were collected and analyzed as a group within a few hours after completion of the run.

Solvent loss during batch-sampling runs of less than 24 hours duration was less than 1%. The technique was unsatisfactory for runs in which very rigorous exclusion of air was desired. This is especially true in measurement of the rate of decomposition of RN_2R by the spectrophotometric method since a trace of air interferes with the measurement presumably because oxygen forms a complex with RR'. For experiments involving oxygen scavenging, batch-sampling was the only applicable technique. Oxygen was bubbled through the reaction mixture during the entire course of the reaction.

Sealed Tube Experiments.—Ampoules were prepared by constricting 150 × 18 mm. culture tubes. Samples from a stock of the reaction mixture were placed in the tubes and the latter were attached to the outlets of a simple manifold by way of rubber stoppers, three way stopcocks and short sections of rubber tubing. During the filling of the tubes care was exercised to avoid contamination of the constricted neck of the ampoule with the reaction solution. The samples were degassed by five freeze-pump-thaw cycles with freezing and pumping at −78° and thawing at room temperature. Finally, the evacuated ampoules were sealed while immersed in the cooling bath. The sealed ampoules were kept in Dry Ice until before the start of a run. Measurement of the spectra before and after degassing showed that no appreciable loss of solvent had occurred.

Just before a run was started the samples were placed in a wire basket and allowed to warm to room temperature. The basket was submerged in the bath and shaken manually for 1 minute. Zero time for the run was taken as 2 minutes after the samples were placed in the bath, and one ampoule was removed at that time. Ampoules were removed at intervals and stored in Dry Ice. Within 5 or 6 hours after the end of the run all samples were analyzed as a group.

Spectrophotometric Analyses.—The absorbencies of RN_2R solutions at 3500, 3600 and 3700 Å. were found to be linear with concentration between 2×10^{-3} and 5×10^{-2} mole l.$^{-1}$. For measurement of the rates of decomposition of RN_2R the initial concentrations were 4-5 × 10^{-2} molar. Absorbencies of chlorobenzene solutions of RR' and RR were measured. At 3700 Å. the value of ϵ for RR' was 0.005 and that of RR was less than 0.01. During the decomposition of RN_2R the absorbence of solutions approached a limit between 0.015 and 0.020. A small correction was applied to readings taken late in the run to determine the concentration of residual RN_2R.

Chlorobenzene solutions of both iodine (0 to 2×10^{-3} molar) and bromine (0 to 5×10^{-3} molar) obey Beer's law at their long wave length absorption maxima, found, respectively, at 5100 and 4400 Å. No other materials involved in the study absorb at these wave lengths.

Both ultraviolet and visible spectral measurements were performed with a Beckman model DU spectrophotometer using constant slit widths.

The ketenimine has a strong, sharp absorption band at 2020 cm.$^{-1}$. No other compounds used or formed in this work have appreciable absorption at this wave length. Empirical calibration curves for optical density *versus* concentration were determined each time a set of samples was analyzed. The amounts of RR' were determined by interpolation from the calibration curves. Measurements were made with a Perkin-Elmer model 21 recording spectrophotometer using a sodium chloride prism and a single pair of matched, 1-mm. cells.

Decomposition of (RN_2R).—One preliminary kinetic run was carried out in *n*-heptane in order to determine optimum conditions for preparation of RR'. All other runs were done in chlorobenzene. *n*-Heptane containing 0.0206 molar RN_2R heated under reflux (98.4°). At appropriate time intervals samples were withdrawn with a hypodermic syringe, transferred to a test-tube, and cooled with ice-water. The optical densities of the samples at 2020 cm.$^{-1}$ were measured. The maximum concentration of RR' was 40% of the original charge of RN_2R, and the maximum occurred between 7 and 8 hours.

In chlorobenzene at 80° the rate of decomposition of RN_2R was determined by manometric monitoring of the rate of nitrogen evolution. The data were fitted to the integrated form of the first-order law by the method of least squares. The rate was also determined at 80° by spectrophotometric analysis for residual RN_2R using the sealed-tube technique. The results of the measurements by the two methods agreed very well. Only the spectrophotometric method was used at 100°.

Initial Rates of Formation of RR' from RN_2R were determined under various conditions: (1) in evacuated sealed tubes and by sampling batch reactions kept under nitrogen, (2) in the presence of oxygen and DBPC, (3) in the presence of DPPH, (4) in the presence of HDPPH and (5) under oxygen with no added antioxidant. Measurements of the rate of RR' formation were made as described above. Relatively high initial concentrations of RN_2R were used in experiments designed to measure initial slopes in order to increase the accuracy in RR' determination at low conversions. At 80° only the early stages of the reactions were studied. At 100° the reaction rates were fast enough to permit monitoring of the whole course of the reactions within a period of a few hours. Reactions in the presence of DPPH and HDPPH were carried out by batch sampling at 80° and in sealed ampoules at 100°. Because of the limited solubility of the scavengers, only the early portions of the runs could be studied before the scavengers were exhausted. No RR' was observed when the decomposition of RN_2R in the presence of oxygen, with no added antioxidant, was followed over a period of 24 hours at 80°. Instead of showing absorption at 2020 cm.$^{-1}$, a new peak appeared at 1692 cm.$^{-1}$ and

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(17) Microanalysis by Dr. A. Elek.

increased in intensity throughout the course of the experiment.

Decomposition of RR'.—All the runs without scavengers were made using sealed ampoules except for one run at 100° which was conducted under a nitrogen atmosphere by the batch-sampling technique. The rate constants obtained by the two techniques agree well as is shown by Table II. Decomposition under oxygen at 100° could be performed only by batch sampling. Decomposition at 80° was too slow to make batch sampling feasible because excessive amounts of solvent were lost to the gas stream during the periods necessary to obtain good rate constants. Therefore, rates were not measured in the presence of oxygen at 80°. The sealed-tube technique was used to study decomposition of RR' in the presence of DPPH and HDPPH.

Efficiency of Radical Production from RN_2R and RR'.—Efficiencies measured by the oxidation method utilized essentially the same procedure as was described earlier.[6] The reaction mixtures consisted of 4 ml. of chlorobenzene and 2 ml. of cumene containing small amounts of initiator (0.5–1.0 $\times 10^{-3}$ molar) and inhibitor (1.0–2.0 $\times 10^{-5}$ molar DBPC). The ratio of the amount of initiator to inhibitor was so adjusted that $kt_l << 1$, where k is the rate of decomposition of the initiator and t_l is the inhibition period. A 50:1 ratio of initiator to inhibitor was suitable at 80°. It was convenient to add the inhibitor as an aliquot from a stock solution in benzene and the initiators were added either as solids or in solution. The rate of oxygen uptake was measured long enough to determine the steady rates of oxidation after the inhibition periods.

The rate of radical production from RN_2R was also measured by the iodine method.[7] The rate of disappearance of iodine was followed spectrophotometrically and was found to be zero order with respect to the iodine concentration. All runs at 80° were carried out by the batch-sampling technique Both $[I_2]_0$ and $[RN_2R]_0$ were varied from run to run in such a way as to maintain the condition, $kt_l << 1$, and to keep t_l large enough to measure with precision. The rate of decomposition of RN_2R at 100° was so fast that satisfaction of the condition $kt_l << 1$ would require t_l to be too short for accurate measurement. Therefore, a was estimated either by using the integrated expression for $[RN_2R]$ or by measuring the rate of disappearance of I_2 early in the run (see Results section). The sealed-tube technique was used since this procedure facilitated accurate timing of sampling at short intervals. In runs in which t_l was determined many samples were taken in order to provide data for meticulous documentation of t_l. Plots of $[I_2]$ *versus* time curved appreciably because of the substantial decay of RN_2R over the course of a run.

Decomposition of RN_2R in the Presence of Bromine.—Runs at 80° were followed by the batch-sampling technique under nitrogen. Samples were withdrawn every 5 to 7 minutes and were analyzed spectrophotometrically for bromine. Experiments were discontinued after the bromine was completely gone. The plots of $[Br_2]$ *versus* time were almost linear. However, b-values calculated from the equation $b = [Br_2]_0/[RN_2R]_0kt_l$ were usually greater than one and showed far less reproducibility than was obtained in measurements of a by the iodine method.

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The Mechanism of Decomposition of Azo Compounds. II. Cage Effects in the Decomposition of α,α'-Azoisobutyronitrile and Related Compounds

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The rate of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') from α,α'-azoisobutyronitrile (RN_2R) has been studied in carbon tetrachloride, benzene and styrene. A particularly detailed study was made in carbon tetrachloride solution at 62.5°. The yield of tetramethylsuccinonitrile (RR) from RN_2R in the presence of bromine has also been estimated. The results, coupled with other available information concerning the decomposition of RN_2R and RR', show that the ketenimine is produced by coupling of both primary and secondary decomposition fragments. Application of the theory of the cage effect as an important part of the mechanism of decomposition of azonitriles and ketenimines is justified.

There have been a number of studies of the rate[2,3] of decomposition of α,α'-azoisobutyronitrile (ABN, RN_2R) and of the rates at which radicals are produced[4–7] during the decomposition using variations of the scavenger lifetime method. The latter studies all show that the decomposition is measurably inefficient in producing radicals.[6,8] The same conclusion has been indicated by study of ABN as an initiator for vinyl polymerization[9–11] and by product analysis under various conditions.[10c,12,13] The principal final product of decomposition in inert solvents is tetramethylsuccinonitrile.[12] However, it is also known that substantial amounts of dimethyl-N-(2-cyano-2-propyl)-ketenimine (RR') are formed and decomposed during the reaction.[14–16]

We have continued our study of this system by following the formation of RR and RR' from ABN. Much of the work parallels that reported in the accompanying paper[17] for the system based on 1,1'-azocyanocyclohexane. All of the equations developed for the latter system are applicable to the ABN problem and will be used in this presentation without repetition.

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